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# The Influence of Plasticizer on Extruded Thermoplastic Starch

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This paper describes the use of an extruder for the plastification process of potato starch with glycerol and water as plasticizers. The influence of both plasticizers is expressed in the water absorption index (WAI) and water solubility index (WSI). The amount of water added prior to extrusion is a tool to protect the starch polymers from degradation and to improve the extruder performance.

## INTRODUCTION

Extrusion cooking is a widely known process used in the food industry. In non-food applications a growing interest exists in the production of thermoplastic starches that can be used as a biodegradable substitute for disposable plastics. For that purpose, starch is extruded with high viscous plasticizers like glycerol or sorbitol, leading to amorphous, transparent, and remeltable plastic masses.

In order to obtain an amorphous thermoplastic mass from starch the structures in the granules have to be disordered. Donovan (1) describes three order-disorder transitions during starch gelatinization. Gelatinization entails 1) the loss of crystallinity of the granule, 2) an uptake of heat as the confirmation of the starch is altered, and 3) hydration of the starch, accompanied by swelling of the granule and decrease in relaxation time of the water molecules. These processes take place simultaneously, or nearly so. The classical gelatinization models in which starch is heated in excess water under shearless conditions are not applicable for the extrusion cooking process. The two main differences are the low moisture content and the high viscosity used in extrusion cooking. During extrusion cooking both temperature and shear are contributors to starch gelatinization. The viscosity of the melt is higher at lower moisture contents resulting in an increased mechanical shear stress and thus an increased degree of gelatinization. Wang (2) states that during extrusion cooking of starch under low moisture, high temperature and high shear circumstances, starch granules undergo both gelatinization and melting processes. The existence of melting and gelatinization at low moisture content is also found in DSC experiments in absence of shear (1,3). Wang (4) also found that shear energy is more efficient in cooking starch than thermal energy.

According to Lawton (5), the basic principles of plastification and gelatinization are the same, i.e., conversion of a solid material to a fluid state by application of heat and shear. Plastification by water depresses the  $T_g$  and the melt viscosity (6). Also, the degradation process can be compared with synthetic polymers. For these polymers shear stress was the major factor in polymer degradation. An increase of temperature results in lower viscosity, and therefore the mechanical degradation decreases (7). Lawton (5) reported that as a result of gelatinization, starch granules become more susceptible to shearing (mechanical degradation) particularly in an extrusion process. The distinct granule structure can break down to produce a homogeneous mixture of fragmented polymers. Colonna (8) found macromolecular degradation of both amylose and amylopectin due to twin-screw extrusion cooking, resulting in lower molecular weight material. Gomez (9) describes a model that proposes mechanical disruption of granules and starch polymers.

The gelatinization and degradation of the extruded thermoplastic starch can be monitored by determining the water absorption index and the water solubility index. The water absorption index (WAI) is an indication for the disordering of the molecular structure. The WAI depends on the availability of hydrophilic groups that bind water and on the gel-forming capacity of macromolecules (10). The WAI passes through a maximum that coincides with essentially complete particle disruption and the gelatinization of the constituent starch granules (11). The water solubility index can be regarded as an index of the degree of macromolecular degradation. Jackson (12) found that the fraction soluble starch consists of individual molecules or loose aggregates. Extrusion cooking under mild circumstances (low viscosity, low temperatures) can yield a product that is not completely gela-

tinized (moderate WAI, low WSI); cooking under severe conditions leads to degradation of the product (low WAI, high WSI).

In previous experiments, mixtures of starch and glycerol (starch contents between 70% and 80%) yielded suitable thermoplastic starch, although the material was not always completely gelatinized. A major disadvantage of these runs was the very high viscosity. The torque upper limit of the extruder was a limitation for experiments with lower glycerol percentages. Apart from the high energy input needed to achieve industrially interesting throughputs, the high viscosity leads to high shear forces and due to viscous dissipation to locally high temperatures. In this study small amounts of water were added prior to extrusion to decrease the viscosity, the high shear forces and the high temperatures in order to reduce polymer degradation during thermoplastic starch extrusion. Removal of the water at the end of the extrusion process is possible, due to the high temperatures of the melt. The percentages of starch and water are varied and the influence of these two parameters on the water absorption index and the water solubility indexes are investigated.

## MATERIALS AND EXPERIMENTS

Food-grade potato starch was obtained from AVEBE, Veendam, The Netherlands. The initial water content was 18%. Technical-grade glycerol (Chemp-roha, Chemical Distrutors, Zwijndrecht, The Netherlands) was used as plasticizer. Distilled water was used during extrusion and analyses.

The extruder used in this study was an APV Baker, corotating and intermeshing twin-screw machine with a screw diameter of 50 millimeters. Starch was fed into the extruder with a Hethon hopper at a feed point

73.5 cm from the die. Water and glycerol were injected 62.5 cm from the die-end with a Santorac 50 pump and a MLP pump, respectively. An outline of the screw lay-out, the feeding points, and the wall temperatures, is shown in Fig. 1.

Only three temperature zones at the die-end of the extruder were heated. The other zones were kept at 30°C to ensure a good and stable transportation and pre-mixing of the feed materials (starch, glycerol and water). At the die-end the wall temperature of the extruder was kept at 150°C, as a result of which a large part of the added water evaporates. A die plate with two capillaries (diameter 3 mm) was used. The screw speed was kept constant at 110 rpm. The total amount of glycerol and starch fed was 13.75 kg/hr during all experiments. Four different ratios of starch/glycerol (80/20, 82/18, 84/16 and 88/12) were used. The amount of water added varied from 0 to 6.4 kg/hr, resulting in a variation of the total amount of plasticizer (water + glycerol) between 20% and 40%. At each experiment, samples were taken after the extruder had reached steady state. The die pressure and torque were recorded.

To determine the complete gelatinization of the extruded thermoplastic starch the material was examined under a microscope (magnification  $16 \times 20$ ). Polarized light was used in order to detect non-gelatinized granules by their birefringence.

The water absorption index (WAI) and the water solubility index (WSI) were determined according to the modified method of Anderson (13). Samples of approximately 4 g of the extruded products were put in liquid nitrogen and ground in a mill to particles of less than 1 mm. The samples were dried overnight in a vacuum oven at 50°C to evaporate any residual water. Subsequently the samples were equilibrated at

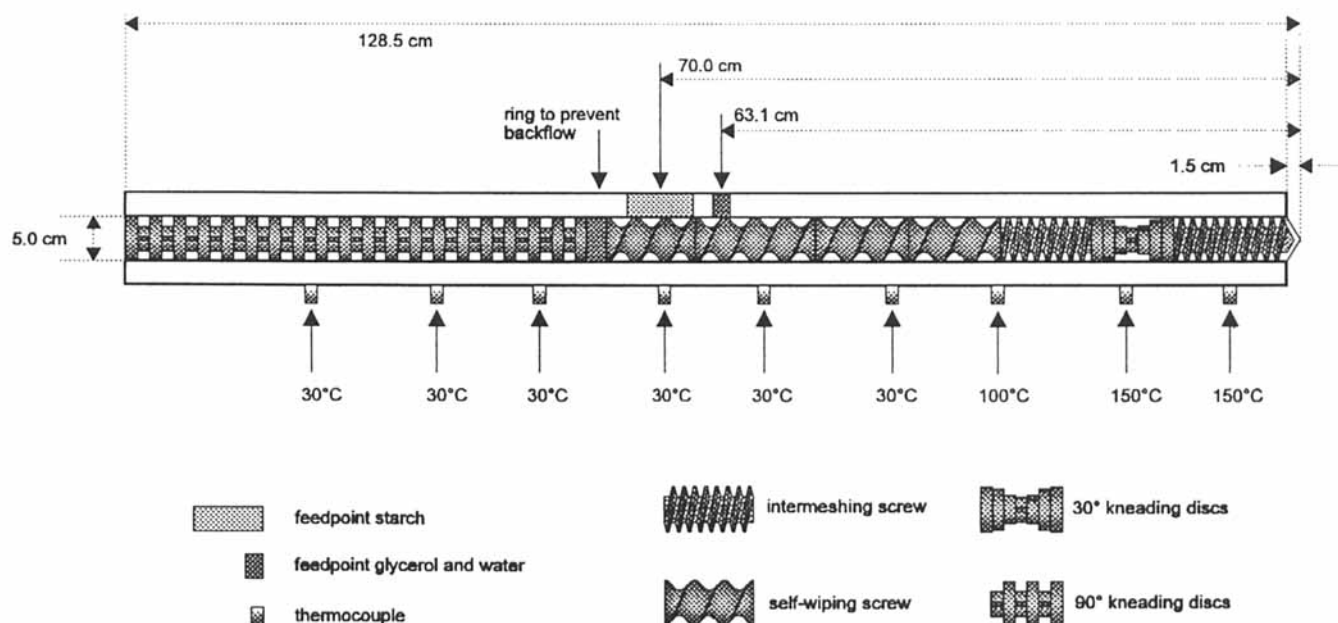


Fig. 1. Screw configuration, feedpoints, and temperature setpoints.

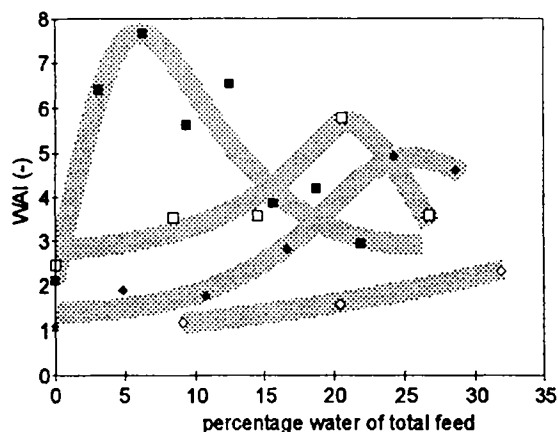


Fig. 2. The effect of the water content prior to extrusion on the WAI at 4 different starch:glycerol ratios: ■ 80/20; □ 82/18; ◆ 84/16; ◇ 88/12.

atmospheric humidity. Amounts of 2.0 g of the material were dissolved in 25 ml water and stirred for 30 min. Hereafter the samples were centrifuged at 9000 g for 15 min. Instead of 3000 g (as described by Anderson) we used 9000 g to obtain a sufficient separation between gel and solution. After centrifuging the gel sediment was weighed and the supernatant was decanted. The dry solids in the supernatant solution were determined by reducing the water content by film evaporation followed by evaporation of the water in a vacuum oven at 135°C overnight. The solids were weighed. The indices are defined by:

$$\text{WAI} = \frac{\text{weight of sediment}}{\text{weight of sample}} \quad (1)$$

$$\text{WSI} = \frac{\text{weight of dissolved solids in supernatant}}{\text{weight of sample}} \times 100 \quad (2)$$

## RESULTS

Under polarized light, all samples showed negligible amounts of birefringence. This indicates complete gelatinization.

The WAI for the series with a fixed ratio between starch and glycerol and a varying water content during extrusion are given in Fig. 2. Notable are the WAI-peaks in the series with high glycerol contents (starch/glycerol ratios of 80/20, 82/18 and 84/16) that occur at 6%, 21%, and 26% water in the feed. These peaks do occur at an increasing amount of water content when the percentage of glycerol decreases. The WAI maximum increases with decreasing starch/glycerol ratios. Table 1 shows that before the WAI-maximum is reached, the WAI of products increase with a decreasing starch/glycerol ratio but with the same percentage of total plasticizer. At high starch/glycerol ratios, the WAI is close to one, indicating that almost no water was absorbed.

The WSI of the samples extruded with varying water content are given in Fig. 3. For lower starch/glycerol ratios, the WSI decreases as the percentage water in the feed increases. For the same percentage water in the feed the samples with a higher starch/glycerol ratio show a higher WSI. A high WSI indicates a higher level of degradation. When the WSI is plotted against the WAI (Fig. 4) we see a continuous decrease of WSI with an increase of WAI.

The influence of the water content on the die pressure is shown in Fig. 5. Each series has constant amounts of starch and glycerol; only the amount of water added prior to extrusion is varied. Between the different series, the ratios between starch and glycerol differ. Two trends can be distinguished: one in which the die pressure decreases with decreasing ratio starch/glycerol, the second shows decreasing die

Table 1. Experimental Data.

Ratio Starch/glyc	Starch (%)	Glycerol (%)	Added Water (%)	Added Plasticizer (%)	WAI (-)	WSI (%)	Torque (Nm)	Die Pressure (10 <sup>5</sup> Pa)
80/20	62.5	15.6	21.9	37.5	2.94	15.33	6250	20.67
80/20	65.0	16.3	18.7	35.0	4.20	8.37	6500	21.36
80/20	67.5	16.9	15.6	32.5	3.87	19.84	7250	26.18
80/20	70.0	17.5	12.5	30.0	6.55	14.08		
80/20	72.5	18.1	9.4	27.5	5.63	17.46	8250	29.63
80/20	75.0	18.7	6.3	25.0	7.68	11.94	8250	31.01
80/20	77.5	19.4	3.1	22.5	6.41	19.20	8250	29.63
80/20	80.0	20.0	0.0	20.0	2.11	61.48	9000	33.07
82/18	60.0	13.3	26.7	40.0	3.58	9.30	6250	27.56
82/18	65.0	14.4	20.6	35.0	5.79	6.07		
82/18	70.0	15.5	14.5	30.0	3.57	38.46	9500	35.83
82/18	75.0	16.6	8.4	25.0	3.52	43.78	10000	42.03
82/18	82.0	18.0	0.0	18.0	2.46	56.57	10750	44.79
84/16	60.0	11.4	28.6	40.0	4.63	1.96	8000	28.25
84/16	63.8	12.1	24.3	36.4	4.94	26.43	8000	28.25
84/16	70.0	13.3	16.7	30.0	2.81	48.22	10000	39.96
84/16	75.0	14.3	10.7	25.0	1.77	70.53	11250	48.23
84/16	80.0	15.2	4.8	20.0	1.90	72.38	12000	44.79
84/16	84.0	16.0	0.0	16.0	1.07	78.95	12000	44.79
88/12	60.0	8.1	31.8	40.0	2.33	70.94	8250	34.45
88/12	70.0	9.5	20.5	30.0	1.57	75.96	12500	55.12
88/12	80.0	10.9	9.1	20.0	1.18	75.59	14500	55.12

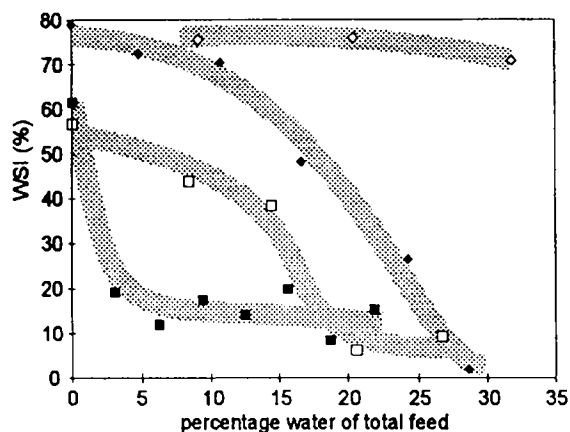


Fig. 3. The effect of the water content prior to extrusion on the WSI at 4 different starch:glycerol ratios: ■ 80:20; □ 82:18; ◆ 84:16; ◇ 88:12.

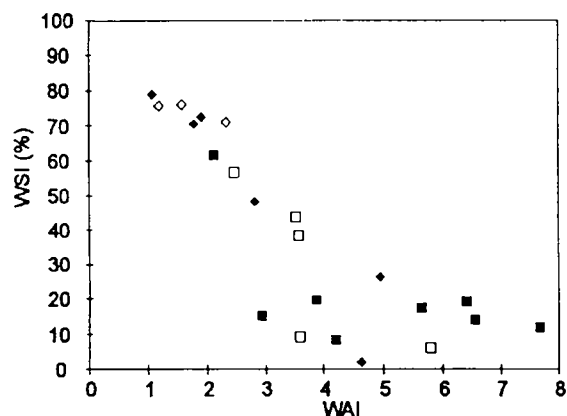


Fig. 4. The water solubility index plotted against the water-absorption index at 4 different starch:glycerol ratios: ■ 80:20; □ 82:18; ◆ 84:16; ◇ 88:12.

pressure with increasing water content. Two series show a plateau at lower plasticizer contents. The torque plotted against the water content showed the same trends as the die pressure but less pronounced.

## DISCUSSION

The interaction diagram in Fig. 6 shows a schematic overview of influence of the water content on the WAI and WSI. All samples showed complete gelatinization under polarization microscopy. This is also indicated by the decreasing WSI with increasing WAI (11). These two results indicated complete gelatinization of the starch. Thus, all effects in WSI, WAI, and die pressure are caused by differences in degradation or water content. Although all the samples are completely gelatinized, the WAI curves show optima. The part left from the maximum can be explained by degradation. The increase of the WAI with decreasing water content right from the maximum may be due to the faster transportation of water to the interior of the physically degraded starch granules as described by Burros (14). Glycerol prevents the starch polymers from degradation; at the same plasticizer content the WAI rises with

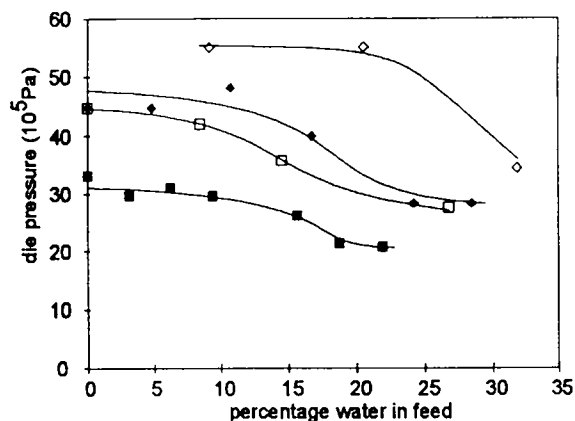


Fig. 5. The effect of the water content prior to extrusion on the die pressure at 4 different starch:glycerol ratios: ■ 80:20; □ 82:18; ◆ 84:16; ◇ 88:12.

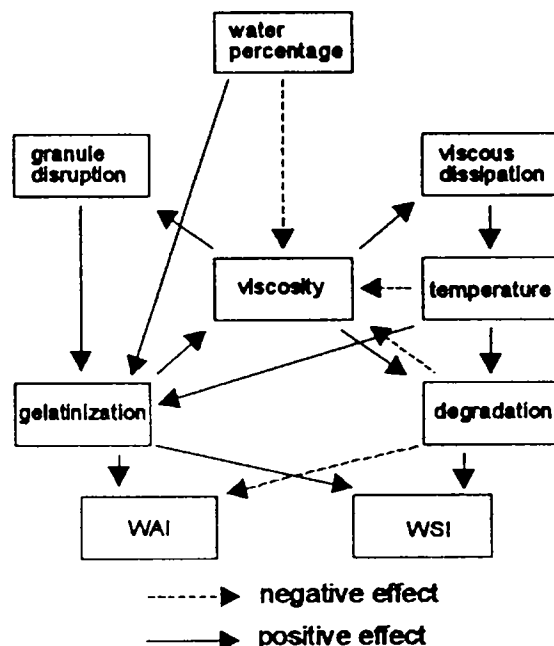


Fig. 6. Interaction diagram of gelatinization and degradation of starch.

a rising glycerol content (Table I). At higher ratios the maximum in the WAI peak shifts to higher water content. More water is needed to obtain the same protection against polymer degradation as glycerol can provide.

The WSI results also show a decrease of polymer degradation with increasing glycerol content. In these experiments the WSI includes the part of glycerol that is leached out of the extruded material. At a low starch/glycerol ratio, more glycerol will leach out. The WSI contains a part that is determined by the degradation of the material and a part that is determined by the percentage of glycerol. We can distinguish three regimes in the WSI plot (Fig. 3), starting at high percentage water prior to extrusion. The first regime is a plateau determined by the amount of glycerol leaching

out of the material, very little degradation is determined (see ratio starch/water = 80/20). The water contents at which the WAI peaks are observed coincide with the end of this plateau. This indicates the beginning of degradation as the WAI peaks occur. The second is a regime in which the degradation increases with decreasing water content. The third regime is a plateau with a high degree of degradation (see ratio starch/glycerol = 88/12). Jackson (12) reported that some depolymerized or retrograded products of starch extruded at moisture content <15% are less soluble in water as individual molecules. This can explain the existence of the plateau.

As the ratio of starch/glycerol rises, the regimes start at a higher percentage water in the feed. Since in the second regime the WSI decreases with an increasing percentage water in the feed, we can state that in this regime the water protects the starch polymers against degradation. This effect is also observed by Gomez (9) and Mercier (15). Owusu (16) reported an opposite effect. Glycerol shows an even better protection-effect than water, at the same plasticizer content the low starch/glycerol ratios give a lower WSI (see Table 1) and thus a lower degree of degradation. Glycerol may act as plasticizer and lubricant. Degradation shortens the polymer length and thus lowers the viscosity. Fritton (17) describes a correlation between intrinsic viscosity and water solubility index for extruded starch. As the starch degradation increases, the intrinsic viscosity decreases and the water solubility increases.

The effect of the water content on the die pressure and torque can be explained as follows. As can be seen in Fig. 6, a lower water content initially results in a higher viscosity. This occurs at intermediate water contents and stems from the decrease in torque and die pressure. At high starch/glycerol ratio and low water content this effect on the die pressure is counterbalanced by degradation, resulting in a plateau. The plateau at higher water content can be caused by faster gelatinization and therefore a longer gelatinized length in the extruder with higher viscosity and more degradation. For the torque the counterbalancing is less evident, because the torque is a measure for the average viscosity over the length of the screw.

## CONCLUSIONS

Glycerol and water both protect starch polymers against degradation during the extrusion process of

thermoplastic starch. Glycerol shows the largest effect, but the percentage of glycerol in the product is determined by the product demands. The addition of water prior to the extrusion process diminishes the degradation of the starch polymers caused by high shear forces. Most of the excess water is evaporated at the die-end of the extruder. The extruder showed improved performance under conditions of lower torque and die pressure. Without adding water the upper torque limit is almost reached and therefore the possibilities to change the extrusion parameters are enlarged by adding water at the feed.

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